

## Surface Water pCO<sub>2</sub> Measurements from Ships

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### Project Summary:

The oceans are the largest sustained sink of anthropogenic carbon taking up on average about  $1.6 \times 10^{15}$  gram (= 1.6 gigaton) of carbon each year. Changes in this sink will be determined by monitoring regional and seasonal patterns of carbon uptake and release. Determination of regional sources and sinks of carbon dioxide in the ocean are of critical importance to international policy decision making, as well as for forecasting long term climate trends. In this project NOAA investigators and academic partners are outfitting research and commercial vessels with automated carbon dioxide analyzers as well as thermosalinographs (TSGs) to measure the temperature, salinity and partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) in surface water and air in order to determine the carbon exchange between the ocean and atmosphere. While this is the largest coordinated effort, it is by no means the only one. Success in constraining the sources and sinks depends critically on international coordination and partnerships. This task is coordinated at national level with the U.S. Carbon Cycle Science Program and its subcommittee on Ocean Carbon and Climate change (OCCC). We work with the International Ocean Carbon Coordination Project (IOCCP) for international coordination. Collaborative efforts are underway to combine datasets in the Atlantic through a Memorandum of Understanding with the European Union project CarboOcean. Pacific collaboration is established through the PICES working group 13. In addition there are one-on-one interactions with investigators in Iceland, France, the United Kingdom, Australia, New Zealand, and Japan on reciprocal data exchange and logistics support.

Documenting carbon sources and sinks relies critically on other efforts undertaken under sponsorship of the Office of Climate Observations (OCO) including implementation of the ship lines, and moored and drifting buoys. The surface water pCO<sub>2</sub> programs support climate services by providing knowledge and quantification of the radiatively important gas, carbon dioxide. The near-term focus is on completion of the Northern Hemisphere ocean carbon observing system to provide data for quantifying carbon dioxide sources and sinks over the coterminous United States through inverse modeling in collaboration with scientists involved in the atmospheric CO<sub>2</sub> observing system.

The project is a partnership of AOML, AOML/GOOS, PMEL, LDEO of Columbia University, RSMAS of the University of Miami, and the Bermuda Institute of Ocean Sciences (BIOS), formerly known as the Bermuda Biological Station for Research (BBSR). The partners are responsible for operation of the pCO<sub>2</sub> systems on the ships, auxiliary measurements, data reduction, and data management from all ships. The following ships

have  $p\text{CO}_2$  systems on them: NOAA ship *Ronald H. Brown*, NOAA ship *Ka'imimoana*, RVIB *Palmer*, cruise ship *Explorer of the Seas*, container ship *Cap Victor*, container ship *Skogafoss*, container ship *Oleander*, and UNOLS research ship *RV Atlantic Explorer* (ship owned and operated by BIOS) The final datasets are combined and sent to CDIAC for dissemination and archival. All work follows established principles of monitoring climate forcing gases and biogeochemical cycles.

### **FY 2006 Progress:**

#### Acquisitions, deployments and data return:

The main metric for this program is obtaining, reducing, quality controlling and disseminating high quality surface water and marine air  $p\text{CO}_2$  data. The number of cruises with  $p\text{CO}_2$  observations from research ships and VOS that have been completed during the performance period are listed in *Table 1*. Details for each ship are provided below.

SHIP	# Cruises	# Data Points	% Recovery*
R/V Brown	12	47,551	86.1%
M/V Skogafoss	7	31,210	61.0%
Explorer of the Seas	46	67,177	80.0%
RVIB Palmer	7	84,909	98.0%
R/V Ka'imimoana	4	54,537	85.0%
R/V Atlantic Explorer	6 months	38,920	86.1%
M/V Cap Victor	6	96,239	91.0%
M/V Oleander	8 months	63,120	67.6%

*Table 1: VOS Data Summary FY-2006.*

\* The values are to illustrate overall performance of the program. They should be used with caution when making ship to ship comparisons. The number of data points is a function of frequency of measurements, number of cruises and instrument malfunction that differ for each ship. Percent recovery has been determined in different fashion by each investigator ranging from number of data points that could have been obtained if the units had operated whenever the ship was at sea to number of acquired data points that were discarded during quality control.

Four other critical endeavors in support of determining regional fluxes have been completed during the performance period:

1. To assure uniformity in measurements and to expand the effort within NOAA OCO and beyond, a technology transfer has been undertaken in which General Oceanics Inc. of Miami, FL will build the underway  $p\text{CO}_2$  systems to our specifications. Substantial time and effort is involved by participants at AOML and RSMAS to assist in building, trouble shooting and improving instrument design. A prototype has been completed and we will oversee production of the first 12 units and provide product support. Participants in the NOAA project ordered six systems of the first production run.

2. With the retirement of Steven Cook, the GOOS/TSG (thermosalinograph) component is taken over by Gustavo Goni who will lead the installation and maintenance of TSG units aboard three ships of the program: the *Oleander*, the *Skogafoss* and the *Cap Victor*. One key

accomplishment has been the installation of the SEAS 2000 software in the *Cap Victor*. The system, which has been upgraded to a micro TSG and dedicated computer, is currently storing data which is retrieved when the ship is serviced in port. The other two will be upgraded this summer. we will also set up a robust quality control and data management system for temperature and salinity for the ships we use, thereby assuring improved data quality of these critical support measurements for the pCO<sub>2</sub> program. AOML has implemented quality control procedures for historical (delayed mode) and real-time mode observations, based on the ten GOSUD (Global Ocean Surface Underway Data Pilot Project) real time control tests and on additional AOML tests. The quality control tests implemented by AOML are among the most complete for TSG observations, which will assure the quality of the data transmitted to the data centers. The quality control of data in delayed-time mode is already being carried out for three ships of the SOOP. The real-time mode was implemented for the TSG data of the *Explorer of the Seas*: ([www.rsmas.miami.edu/rccl](http://www.rsmas.miami.edu/rccl)).

3. In addition to leading the effort on the *Palmer* the LDEO group has provided two critical data packages towards to overall goal of this project. The data produced by the NOAA-supported groups as well as those from international collaborators from Japan, Iceland, Germany and France, were processed into a single format at the Lamont-Doherty Observatory. A compilation of all coastal data was assembled that is the cornerstone of an assessment of the role of the coastal ocean in carbon dynamics (Chavez and Takahashi, 2006). The comprehensive dataset that was used to create the global pCO<sub>2</sub> climatology comprised of 3 million data points from over a dozen research groups was sent to the Carbon Dioxide Information and Analysis Center (CDIAC) at the Oak Ridge National Laboratory, for the permanent archive and ready access to the public. The data are being examined by the CDIAC staff, and the release date has not been determined pending on the consent of European contributors for releasing their data.

4. The RSMAS group jointly maintains the pCO<sub>2</sub> system on the *Skogafoss* and has analyzed discrete surface samples for Total Alkalinity (TA) and Total Inorganic Carbon (TC) that have been collected on select cruises. These state variables provide the opportunity to further elucidate the factors that control the surface water pCO<sub>2</sub> and can provide a physical basis for the CO<sub>2</sub> flux map analysis.

Several opportunistic collaborations have increased our data holdings. The AOML/GOOS group has provided a TSG for the *Atlantic Companion* maintained by the Leibnitz oceanographic Institute in Kiel. As part of this arrangement this group will share the pCO<sub>2</sub> and TSG data of the line.

A pCO<sub>2</sub> system was lent to Prof. Brain Ward of Old Dominion to outfit a cruise in the North Atlantic. This high resolution data set augments our high latitude data. We continue close interactions with the University of Bergen in data exchange for the North Atlantic and interpretation to improve flux maps in this region.

The responsibilities of the different groups are summarized in the flow diagram below.

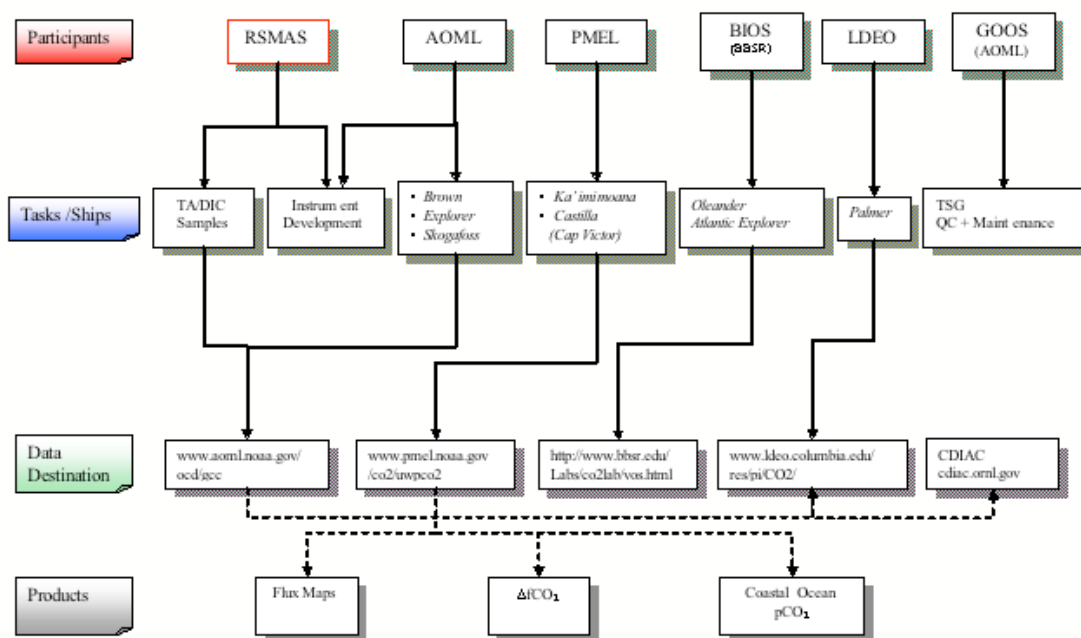


Figure 1: Organizational chart of the VOS project.

A short summary of the efforts on each ship are listed below:

**NOAA ship *Ronald H. Brown*- AOML lead**



**Causes for non-return:** The underway  $p\text{CO}_2$  system on the *Brown* enjoyed over a 85 % data return. Trips had to be made to Boston for fixing a clogged air line and to Charleston to replace a waterbath. The thermosalinograph on the *Brown* yielded poor data on several of the cruises complicating data reduction. Overall returns from the ship continue to be excellent (see *Table I*)

**Description:** The cruise tracks for each cruise of the *Brown* for FY 2005 and FY 2006 are shown at [http://www.aoml.noaa.gov/ocd/gcc/rvbrown\\_data2005.php](http://www.aoml.noaa.gov/ocd/gcc/rvbrown_data2005.php). The cruises include the annual deployment of moorings in the eastern Equatorial Pacific. *Figure 2* shows the trends for three years encompassing the last occupation and a El Niño and La Niña year showing the large changes from year to year. Feely et al. (2006), quantify these fluxes and show that the Equatorial Pacific is the region that contributes most to the flux variability.

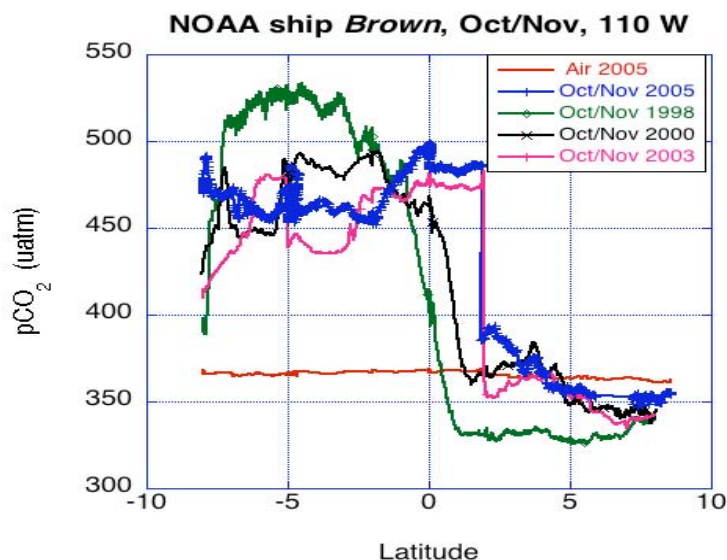


Figure 2:  $p\text{CO}_2$  data from the R/V Brown for the years 2002 to 2005

## NOAA ship *Ka'imimoana*- PMEL lead



**Data Site:** <http://www.pmel.noaa.gov/co2/uw>

**Number of cruises:** 4

**Number of  $p\text{CO}_{2w}$  data points:** 54,537

**% Data return:** 85%.

**Causes for non-return:** The underway  $p\text{CO}_2$  system on the *Ka'imimoana* yielded a 85 % data return during 2005-2006. There were periodic system failures due to problems associated with water vapor removal. There were also problems associated with low water and gas flow. The thermosalinograph information must be integrated into the data files after the cruises, which complicates data reduction.

**Description:** During 2005-2006 the *Ka'imimoana* was involved in studies in the Equatorial Pacific between 95°W and 165°E (*Figure 3*). The cruise data can be obtained from our website located at: <http://www.pmel.noaa.gov/co2/uw>. A summary of the cruise results from November 1997 through August 2006 is shown on the frontispiece and in *Figure 4*. The results show weak seasonal and strong interannual variability of  $\text{CO}_2$  fluxes from the oceans to the atmosphere. These results are described in detail in Feely et al (2006). The most recent data will undergo further contextual checks by LDEO scientists before it is submitted to CDIAC for archiving.

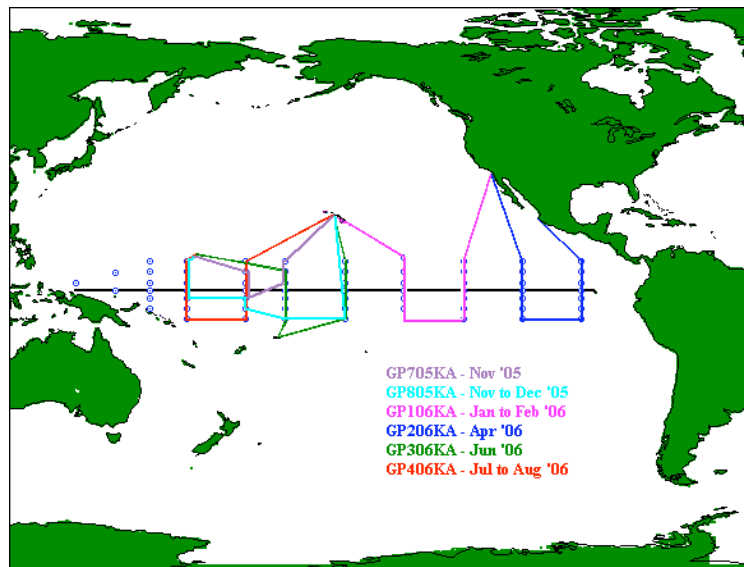


Figure 3: *Ka'imimoana* track lines occupied during FY 2006.

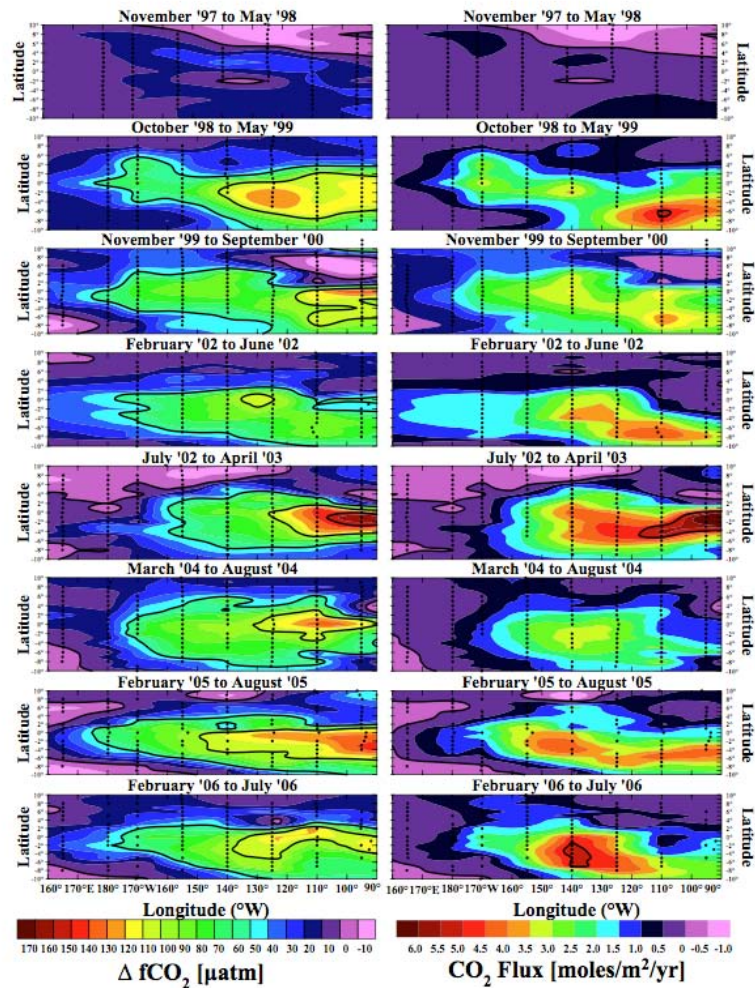


Figure 4: Time-Series of surface water  $p\text{CO}_2$  levels in the tropical Pacific resulting from Ka'imimoana repeat observations from 1997 thru 2006.

### RVIB Palmer- LDEO lead

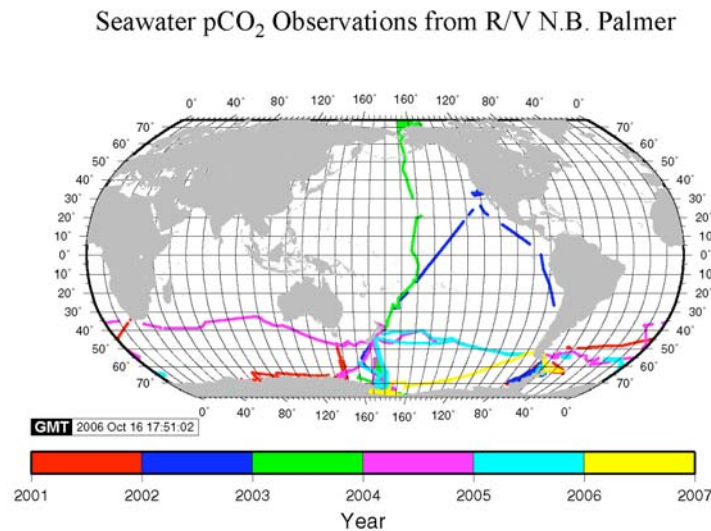




**Description:**

We have operated successfully a semi-automated surface water  $p\text{CO}_2$  system aboard the RVIB *Nathaniel Palmer* with vital operational assistance from the Raytheon Polar Support group. Since RVIB Palmer, an ice-breaking research vessel, is one of the few research ships which are operated in high latitude areas of the Southern Ocean even during winter months, our  $\text{CO}_2$  program aboard this vessel allows us to make observations in hostile environments of the high latitude oceans, where deep and intermediate water masses are formed in winter. During transits to her homeport we have been able to make measurements along long transects over other parts of global oceans. (see *Figure 5*) and an additional 85,000 data points have been processed and added to our database during this 2005-06 funding period. The expeditions of the Palmer during 2005-06 were mostly in the high-latitude Pacific Sector of the Southern Ocean between latitudes  $40^\circ\text{S}$  and  $75^\circ\text{S}$ . We continue to acquire the surface ocean  $p\text{CO}_2$  and associated SST and salinity data aboard the RVIB Palmer during this coming investigation period.

Upgrading of our  $p\text{CO}_2$  system was started two years ago with the support from NOAA. It has been completed successfully for the past two years. More automation has been added, and the at-sea performance of the upgraded system has been excellent



*Figure 5: The locations of surface water  $p\text{CO}_2$  measurements made aboard the RVIB Palmer since 2001. Colors indicate the years when the measurements were made. The 2005-06 observations are mostly in the New Zealand-Ross Sea and Drake Passage areas.*



## Cruise ship *Explorer of the Seas*-AOML lead



**Causes for non-return:** Some loss of data occurred because of water delivery problems to the equilibrator. Because of the shallow intake the seawater entrains air during heavy seas and the system is turned off during these conditions. Slow flushing of lines means that we omit data from the first 10-minutes after the standard run.

**Description:** After four years of sailing in the Caribbean the ship changed its route to sail to Bermuda during the summer time with alternating cruises from New York to Bermuda and from New York to the Eastern Caribbean. During the wintertime the original cruise track in the Eastern and Western Caribbean are occupied. This yields excellent temporal and spatial coverage. The area has been used as a test bed to create flux maps utilizing remote sensing (see research highlights). During the performance period a near-real time data display was instituted where daily pictorial updates of concentrations along the cruise track in color-code like in *Figure 6* below and a display of temperatures and concentrations are provided on the website: [http://www.aoml.noaa.gov/ocd/gcc/explorer\\_realtime.php](http://www.aoml.noaa.gov/ocd/gcc/explorer_realtime.php) for system checks and quality control.



*Figure 6: Summer Cruise Tracks of the Explorer of the Seas with surface water  $p\text{CO}_2$  levels for late summer 2006.*

## Container Ship *Skogafoss*- AOML & RSMAS lead



**Causes for non-return:** This has system run unattended or with untrained observers except for 2 cruises when AOML or RSMAS personnel were onboard. Data gaps have occurred for a variety of reasons, including failure by ship's personnel to open the seawater valves, leaks in the system that caused an automatic shutdown, and a malfunctioning drain pump. The problems have resulted in frequent trips by AOML and RSMAS personnel to the ship.

**Description:** The *Skogafoss* sails between Iceland and Boston and covers a critical high latitude region that has been shown to be a large CO<sub>2</sub> sink. Large seasonal variations are observed as shown in *Figure 7*. During the early spring, pCO<sub>2</sub> values well above atmospheric levels are measured over most of the ocean transect due to entrainment of deep water to the surface. In late spring, values decrease significantly as a result of high biological productivity during this time.

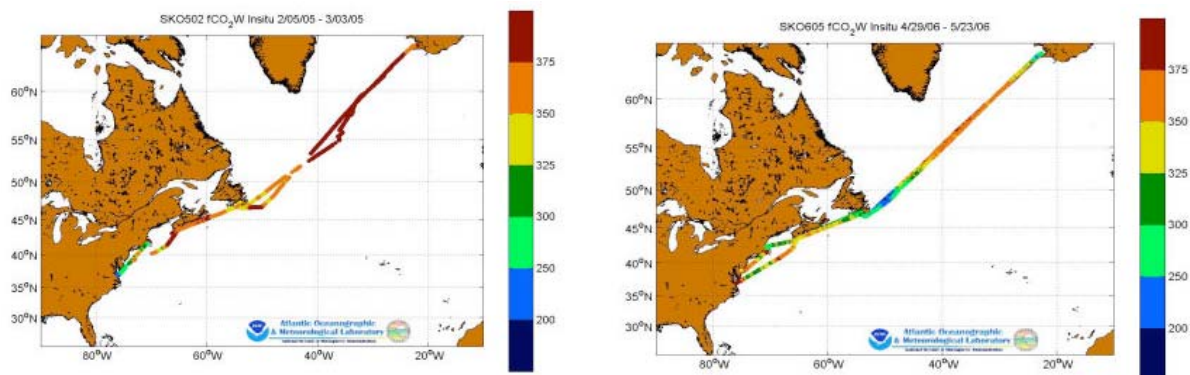


Figure 7: pCO<sub>2</sub> levels along the transect of the *Skogafoss* in February 2005 and May 2006 (figures from [http://www.aoml.noaa.gov/ocd/gcc/skogafoss\\_introduction.php](http://www.aoml.noaa.gov/ocd/gcc/skogafoss_introduction.php))

## Container Ship *Oleander*- BIOS lead



### *Causes for non-return*

The  $p\text{CO}_2$  system was installed on the MV *Oleander* in February 2006. Over the last 8 months, the total data collected was 63,120, with a 67.6% data recovery. The remaining 32.4% had some caveats associated with flow rates through the licor. The MV *Oleander* system uses a LiCOR 7000 NDIR detector, and there are a few minor unresolved issues of comparability to systems with a LiCOR 6262 NDIR detector.

On the MV *Oleander*, the equilibrator is located in the Engine Room near the seawater system and TSG. It is located  $\sim 5'$  below the water line, requiring the equilibrator waste seawater to free drain into a waste reservoir, which in turn will be drained by a new pump back into the seawater line downstream of the tap off to the  $p\text{CO}_2$  system. The pump has failed twice with shutdown of the system after overflow into the ship's bilges. We have added a second, stronger pump to ensure that the waste water is pumped overboard. There have also been several ship power problems. We have installed a UPS line, but the power outage has exceeded the UPS battery life on one occasion. The primary filter on the seawater intake line has also needed to be cleaned each week; otherwise rust and debris from the *Oleander's* internal plumbing clogs the line and slows the flow rate into the equilibrator.

The average temperature of the engine room has been  $\sim 47^\circ\text{C}$  with the CPU failing due to temperatures over  $60^\circ\text{C}$ . We have modified the dry box, adding new fans, and replaced the CPU with one that has a higher temperature threshold. The replacement of the CPU caused a problem with the GPS comport that is currently being addressed. The engine room air is quite dirty requiring cleaning of all filters each week. We have also had problems with the Superlogic Module boards; these modules have had to be replaced. The condenser tubes have clogged with salt crystals causing a shutdown of the system. The condenser tubes have been replaced.

The seawater and atmospheric  $p\text{CO}_2$  data will also be served at the following site (<http://www.bbsr.edu/Labs/co2lab/vos.html>).

**Description:** The MV *Oleander* crosses weekly between New Jersey and Hamilton, Bermuda. Given the ~100 crossings a year, this gives excellent temporal and spatial coverage of the North Atlantic subtropical gyre, Gulf Stream, middle Atlantic Bight and coastal zone. The MV *Oleander* transits the region of Subtropical Mode Water (STMW) formation during the winter southeast of the Gulf Stream, and the highly productive coastal zone of the Eastern Seaboard.

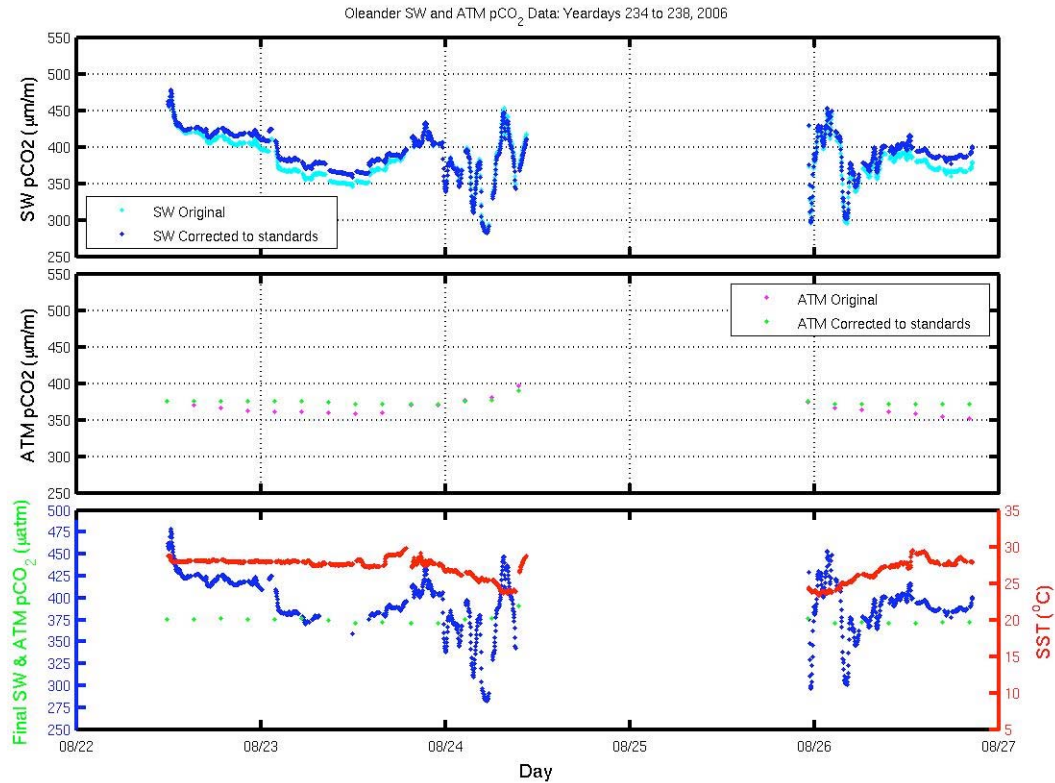


Figure 8: Example of Oleander data during a crossing from New Jersey to Bermuda, and back again in August 2006. The data gap is when the ship on 8/25 was in port

### Atlantic Explorer - BIOS lead



### ***Causes for non-return***

The  $p\text{CO}_2$  system was installed on the RV *Atlantic Explorer* in April 2006. Over the last 6 months, the total data collected was 38,920, with a 86.1% data recovery. The remaining 13.9% were flagged due to problems associated with the Valco multiposition valve and distribution of standards through the system. A permanent airline remains to be installed during the December shipyard visit for the *Atlantic Explorer*.

The major problem with the *Atlantic Explorer* system has been intermittent problems with the Valco multiposition valve. The valve has been replaced. We have had problems with the Ivisco valve that controls the flushing of the lines with freshwater. This valve has failed twice due to salt crystal buildup. We have also had problems with clogging of the flow meter impeller. We have also had problems with the Superlogic Module boards due to faulty power feed; these modules have had to be replaced. The acrodisk have also been clogged and in need of regular cleaning. We have also had a few problems with the GPS system, with a faulty 232 to 424 converter, and faulty comport. The seawater and atmospheric  $p\text{CO}_2$  data will also be served at the following site (<http://www.bbsr.edu/Labs/co2lab/vos.html>).

***Description:*** The R/V *Atlantic Explorer* operates in the North Atlantic Ocean (zone NA6), servicing four oceanographic time-series (e.g., Bermuda Atlantic Time-series Study, Hydrostation S, Bermuda Testbed Mooring, Ocean Flux Program) and other research projects. This data stream provides groundtruthing  $p\text{CO}_2$  datasets for the subtropical gyre of the North Atlantic Ocean. In 2007, the *Atlantic Explorer* is scheduled for 173 days.

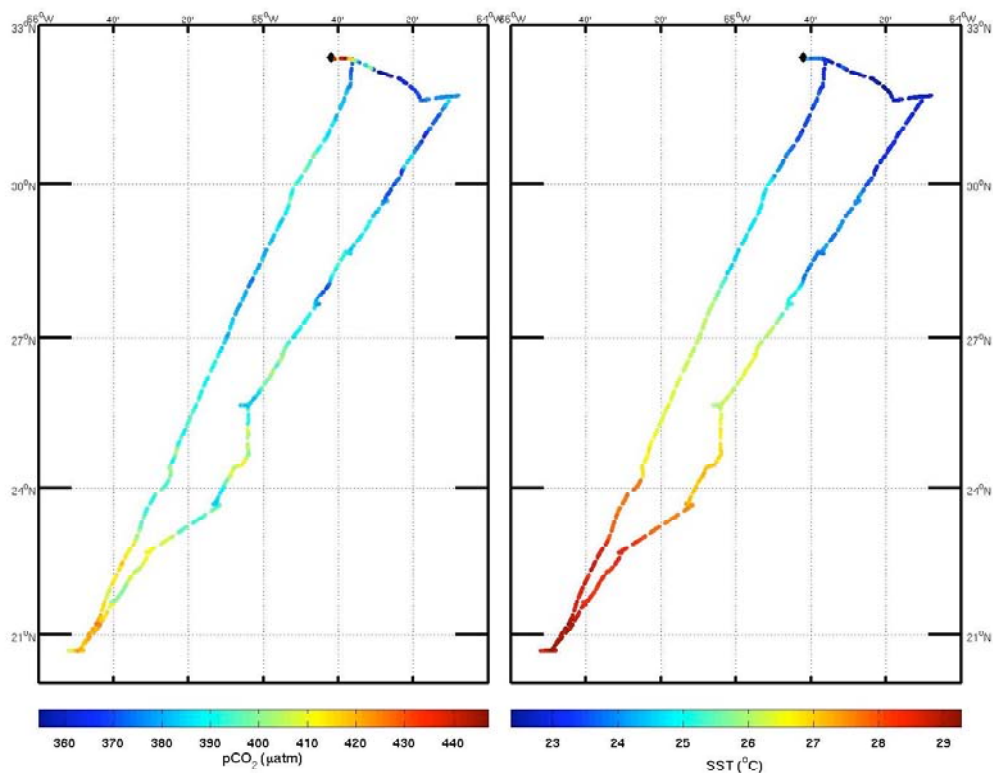


Figure 9: Example of Atlantic Explorer data during a transect across the North Atlantic subtropical gyre in May 2006.

### Container ship *Cap Victor* - PMEL lead



**Causes for non-return:** The underway pCO<sub>2</sub> system on the *Cap Victor* (formerly *Columbus Waikato*) resulted in a 91 % data return during 2005-2006. There were minor system failures due to problems associated with water vapor removal.

**Description:** During the fall of 2005 and 2006 the *Cap Victor* was involved in studies in the tropical and subtropical Pacific (**Figure 10**). This research is done in collaboration with

Drs. Paul Quay of the University of Washington and Bronte Tilbrook of the CSIRO in Hobart, Australia. In addition to supporting our underway pCO<sub>2</sub> measurements, they are also collecting samples for carbon isotope measurements (Quay) and DIC and nutrients (Tilbrook). For this reason, we have combined resources to place ship riders on each of the cruises. They maintain the underway systems and collect the discrete samples. The cruise data can be obtained from our website located at: <http://www.pmel.noaa.gov/co2/uw>.

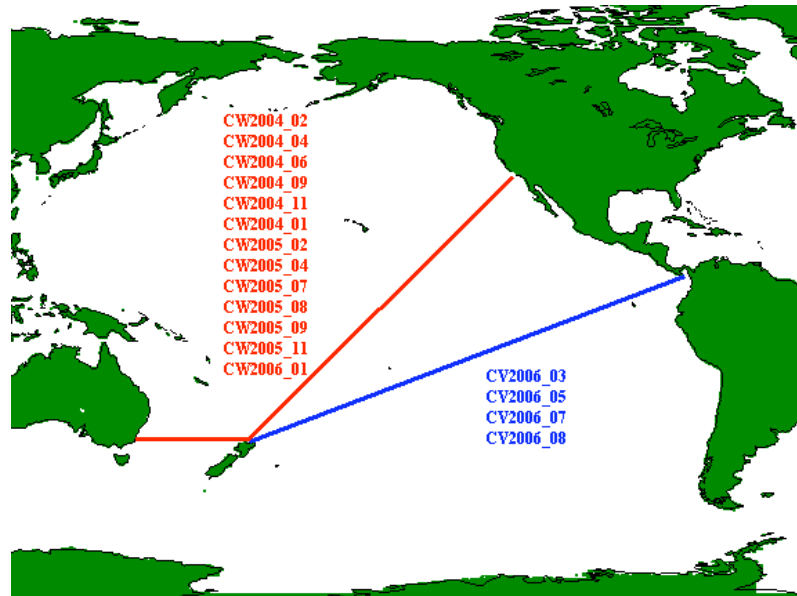


Figure 10: Cruise Tracks of the Columbus Waikato (red) and Cap Victor (blue) occupied during FY2004-2004.

A summary of the cruise results from Fall 2005 thru September 2006 is shown in Figure 11 and Figure 12. The results show strong seasonal variability of CO<sub>2</sub> fluxes in the southern and northern subtropic, but out of phase by 6 months. These results are described in the AGU/ASLO abstract by Cosca et al., (2006). The data will undergo further contextual checks by LDEO scientists before it is submitted to CDIAC for archiving. The *Cap Victor* was relocated to the Atlantic in the Fall of 2006.



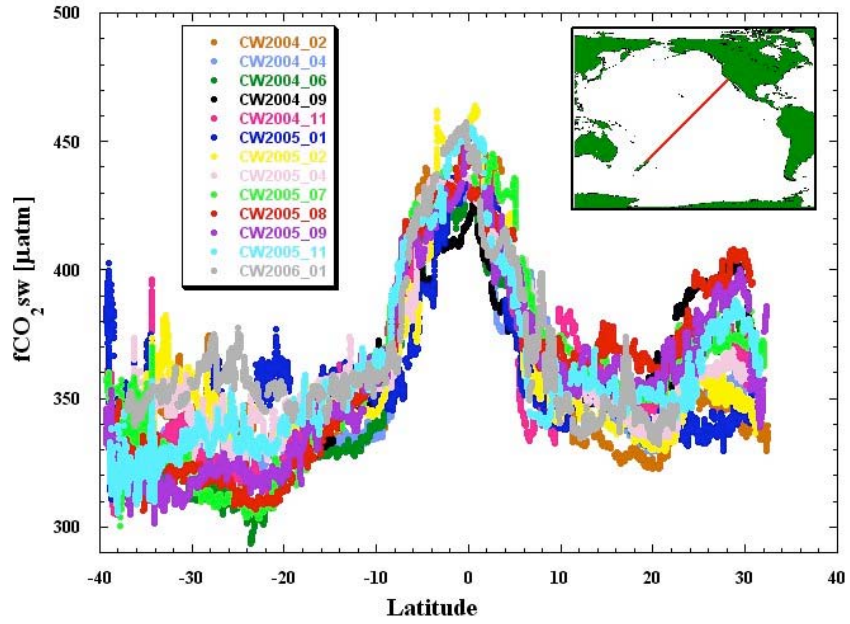


Figure 11: Time-Series of surface water  $p\text{CO}_2$  levels in the tropical and subtropical Pacific Resulting from Columbus Waikato repeat observations from 2004 to 2006..

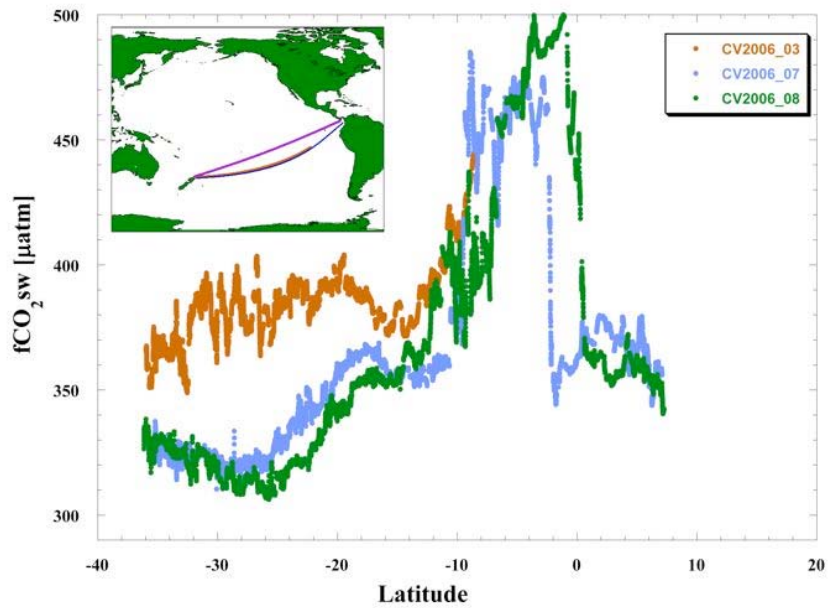


Figure 12: Time-Series of surface water  $p\text{CO}_2$  levels in the tropical and subtropical Pacific Resulting from Cap Victor repeat observations in 2006.

#### Adherence to monitoring principles

The efforts of the NOAA VOS pCO<sub>2</sub> group have met the important monitoring principle of uniform instrumentation with a quantifiable accuracy. All systems are calibrated with standards that are traceable to the WMO scale. The first units were delivered in the summer of 2003, within a year of receipt of program funding. We are actively involved in assuring uniform instrumentation, through a technology transfer with the manufacturer General Oceanics who is building instruments to our specifications, uniform operating protocol, and uniform data reduction procedures.

#### Data management and dissemination:

An important part of the VOS effort is to disseminate quality controlled data to the community at large in an expedient fashion.

For the thermosalinograph data the AOML/GOOS group developed a data quality control computer code using OpenSource, FreeSoftware and multiplatform solutions, which allow great freedom for the future of the project. It injects the data into a PostgreSQL database where it is then subjected to different quality control procedures. Probably the major advantage to have the dataset in a relational database, such as PostgreSQL, is the use of indexes for fast sub samples by any criteria, for example QC flags, range limits, time windows or grouped values by sensors or area or ships. On this way, from the same real dataset, could be created virtually infinite metadata sets with the same storage demand and a small development effort. We are planning to install a DAP server, which will allow the direct access to the database from traditional scientific tools, such as MatLab, Python, Grads, Ferret, and others. The core of the system management is done in Python, which has modules for the direct database access, scientific procedures and easily deal with dates between other advantages which allow a robust and fast development. Details on each of the quality control steps can be found in : [www.aoml.noaa.gov/phod/tsg/data/qc\\_sheet.pdf](http://www.aoml.noaa.gov/phod/tsg/data/qc_sheet.pdf).

The LDEO group, in close interaction with the data acquisition groups, oversees shipboard quality control so that the quality of data and consistency is monitored for the whole group. The participants of the VOS program are able to access the data which are listed in an uniform format. For this purpose, the LDEO group established an open web site at the following URL: <http://www.ldeo.columbia.edu/CO2>. The site provides not only the numerical data, but also maps showing the ship's tracks for each data file. The new data will be accessible only to the VOS participants for a set period agreed on by the PIs, and will be sent to the Carbon Dioxide Information and Analysis Center (CDIAC), Oak Ridge, TN, for the permanent archiving and distribution to the public. This close coupling of the data acquisition with data processing/evaluation and interpretation will guarantee high quality field observation data.

As a part of the VOS program, the Lamont group processed and added to its database the measurements made during cruises of the R/V Laurence M. Gould, which is supported by NSF as a part of the Long-Term Research in Environmental Biology (LTRE) program. For the 2005-06 period, the Gould transited across the Drake Passage every month, and these

observations are ideally suited to document seasonal variability in the area. During the present reporting period of 2005-06, about 100,000 new surface water pCO<sub>2</sub> data have been added to the database. A total of 284,000 surface water pCO<sub>2</sub> data have been obtained since the beginning of the program in 2002.

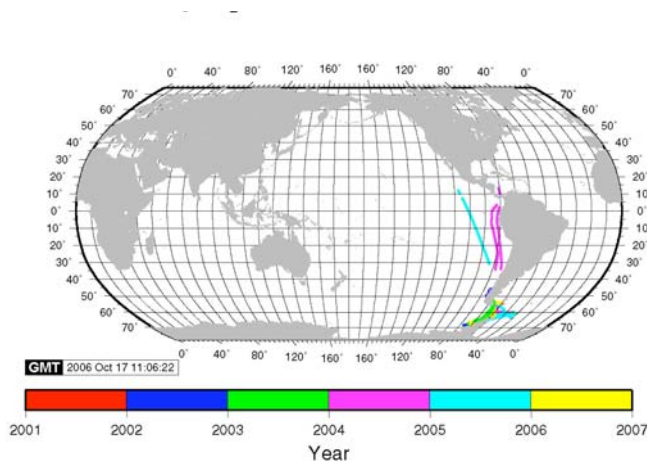


Figure 13: The locations of the surface water pCO<sub>2</sub> measurements obtained aboard the RV Gould during this project, March, 2002 through August, 2006. The years of the measurements are color coded.

During the performance period two important data products were submitted to CDIAC. A compilation of coastal data from this group and other investigators was provided that is the cornerstone for the chapter 17 of the SOCCR report (*Chavez and Takahashi, 2006*). All the data that are used for the global pCO<sub>2</sub> climatology comprised of 3 million data points was sent to CDIAC as well.

CDIAC has just implemented a Live Access Server (LAS) for the data with funding from a companion effort. The LAS at <http://cdiac3.ornl.gov/underway/servlets/dataset> is being populated. Investigators, and the oceanographic community use the data extensively. This data is also used for national and international assessments such as the IPCC.

#### Research highlights:

1. It is widely recognized that robust methods to interpolate CO<sub>2</sub> measurements in time and space are needed to produce CO<sub>2</sub> flux maps from measurements along a line. Publications by *Lueger et al.* (2006) for the North Atlantic and *Wanninkhof et al.* (2006) for the Caribbean Seas show how temperature can be utilized to produce regional flux maps. The algorithms are area specific but show a robust predictive capacity and provide a way to utilize remote sensing to produce flux maps with high spatial and temporal resolution. The data used to create the algorithms were obtained on the ships funded under this effort.
2. Air-Sea CO<sub>2</sub> fluxes in the Caribbean: Air-sea fluxes in the Caribbean Sea are determined from 2002-2005 based on data from an automated system onboard the cruise ship

*Explorer of the Seas*. The partial pressure of CO<sub>2</sub> in seawater, pCO<sub>2sw</sub>, are used to develop algorithms of pCO<sub>2sw</sub> based on sea surface temperature (SST) and position. Regressions are applied to assimilated SST data and remotely sensed winds on a 1° by 1° grid to estimate the fluxes on weekly timescales in the region. The positive relationship between pCO<sub>2sw</sub> and SST is lower than the iso-chemical trend suggesting counteracting effects from biological processes. The relationship varies systematically with location with a stronger dependence further south. Furthermore, the southern area shows significantly lower pCO<sub>2sw</sub> in the fall compared to the spring at the same SST, which is attributed to differences in salinity. The annual algorithms for the entire region show a slight trend between 2002 and 2004 suggesting an increase of pCO<sub>2sw</sub> over time. This is in accord with the increasing pCO<sub>2sw</sub> due to the invasion of anthropogenic CO<sub>2</sub>. The annual fluxes of CO<sub>2</sub> yield a net invasion of CO<sub>2</sub> in the ocean that ranges from -0.04 to -1.2 mol m<sup>-2</sup> yr<sup>-1</sup> over the three years. There is a seasonal reversal in the direction of the flux with CO<sub>2</sub> entering into the ocean during the winter and an evasion during the summer. Year-to-year differences in flux are primarily caused by temperature anomalies in the late winter and spring period resulting in changes in invasion during these seasons (Reference: Wanninkhof *et al.* 2006).

3. As part of our continuing effort to understand decadal changes in the carbon fluxes of the equatorial Pacific, we developed seasonal and interannual pCO<sub>2</sub>-SST relationships from shipboard data that were applied to high-resolution temperature fields deduced from satellite data to obtain high-resolution large-scale estimates of the regional fluxes. The data were gathered onboard research ships from November 1981 through June of 2004. The data were collected during repeat transects of the equatorial Pacific between 95°W and 165°E, and included five El Niño periods (1982–1983, 1986–1987, 1991–1994 and 1997–1998 and 2002–2003) and three La Niña periods (1988–1989, 1995–1996 and 1998–2000). Data were collected during the warm boreal winter-spring season (January through June) and during the cooler boreal summer-fall season (July through December) of each year making it possible to examine the interannual and seasonal variability of the fCO<sub>2</sub>-SST relationships. A linear fit through the data sets yields an inverse correlation between SST and fCO<sub>2</sub>, with both interannual and seasonal differences in slope. In particular, the results indicate a strong interannual El Niño – Southern Oscillation (ENSO), Pacific Decadal Oscillation (PDO) and weaker seasonal variability. There is also a slight increase (~27%) in the out-gassing flux of CO<sub>2</sub> after the 1997–1998 PDO mode shift. Most of this increase is due to increase in wind speeds after the spring of 1998. These increases are consistent with the recent rebound of the shallow water meridional overturning circulation in the tropical and subtropical Pacific after the PDO shift. (Reference: Feely *et al.*, 2006)
4. Using the observations made since the 1970's we have investigated increases in pCO<sub>2</sub> in surface water in the North Pacific Ocean. In 19 areas that are located in the open North Pacific, the surface water pCO<sub>2</sub> values have been increasing at a rate similar to the mean atmospheric CO<sub>2</sub> increase of about 1.5 ppm/yr. Although surface waters are out of equilibrium with atmospheric CO<sub>2</sub> because of the seasonal swing of SST, biological production and deep-water upwelling, the ocean surface waters appear to take up CO<sub>2</sub> from the air keeping up with the atmospheric CO<sub>2</sub> increase. In contrast, in four areas

located near and within the Bering and Okhotsk Seas, the surface water  $p\text{CO}_2$  have been decreasing with time, in spite of the fact that surface water temperatures have been increasing. This may be attributed to an increase in photosynthesis in the high latitude North Pacific, that has been reported by Gregg et al. (2003) on the basis of remote-sensed ocean colors. (Reference: Takahashi et al., 2006)

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